AZO BİLEŞİKLERİNİN HİDRAZIN HIDRAT İLE
REDÜKTİF BÖLÜNMESI VE BAZI YENİ
1,3,4-TIYADİAZOŁ TÜREVLERİ

REDUCTIVE CLEAVAGE OF AZO COMPOUNDS WITH
HYDRAZINE HYDRATE AND SOME NEW
1, 3, 4-THIADIAZOLE DERIVATIVES

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SUMMARY

In this study, the azo groups of 2-aryl/alkylamino-5-[p-(1′
-phenyl-3′,5′-dimethyl-4′-pyrazoly[azo]-phenyl)]-1,3,4-thiadiazoles which
were previously prepared by us were reduced with hydrazine hydrate
without a catalyst in ethanol and the following compounds were
obtained: 2-n-propylamino-5-(p-aminophenyl)-1,3,4-thiadiazole (I), 2-n-
buthylamino-5-(p-aminophenyl)-1,3,4-thiadiazole (II), 2-cyclohexyla-
mino-5-(p-aminophenyl)-1,3,4-thiadiazole (III), 2-phenetylamo-5-(p-
aminophenyl)-1,3,4-thiadiazole (IV), 2-phenylamino-5-(p-aminophenyl)
1,3,4-thiadiazole (V). The structures of these substances were
elucidated using UV, IR and NMR spectral methods besides elemen-
tary analysis.

ÖZET

Bu çalışmada, daha önce tarafımızdan hazırlanan 2-aryl/
alkil-1′-amino-5-[p-1′-fenil-3′,5′-dimetil-4′-pi:azollazo]-fenil]-1,3,4-tiyadi-
azollerin, azo grubu katalizörsüz olarak etanolü ortamda hidrazin

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INTRODUCTION

We have previously reported (1) the synthesis and spectroscopic analysis of 1, 3, 4-thiadiazoles with azo groups. It is known that hydrazine hydrate reduces the azo groups to amino groups in the presence of a catalyst (2). We had observed that hydrazine hydrate also reduced the azo group without a catalyst (3-5).

Owing to our interest in the synthesis of 2-alkyl/arylaminophenoxy-5-(p-aminophenyl)-1, 3, 4-thiadiazoles, we attempted to prepare it by reductive cleavage with hydrazine hydrate.

EXPERIMENTAL

Melting points were taken on apparatus Buchi (Flawil/Schweiz) and are uncorrected. UV spectra were obtained with a 25 Model Beckman recording spectrophotometer. IR spectra were recorded on a Perkin-Elmer 577 Spectrophotometer in KBr. NMR spectra were recorded on a Varian A 60 D instrument using TMS as an internal standard.

General method for the preparation of the compounds

A mixture of the azo compound (0.0025 mol), hydrazine hydrate (3 ml of 99 %) and ethanol (30-40 ml) was stirred for 30-45 min at 60-65 °C. Excess ethanol was removed by distillation, when the water was added to the solution, white or pale yellow crystalline product was obtained and recrystallized from aqueous ethanol (1:1).

2-n-Propylamino-5-(p-aminophenyl)-1, 3, 4-thiadiazole (I)

The substance was prepared according to the general method from 1.03 g of 2-allyl-(zolylazo)phenyl]-1, 3, 4-thi

2 n-Buthylamino-5 (p ar

The substance was prepared from 1.07 g of 2 n-buthyl pyrazolylko(azo)phenyl]-1, 3

2 Cyclohexylamino-5 (p

The substance was prepared from 1.14 g of 2 cyclohex pyrazolylko(azo) phenyl]-1, 3

2 Phenethylamino-5 (p-

The substance was prepared from 1.2 g of 2-phenethyl pyrazolylko(azo) phenyl]-1,3

2-Phenyl-5-(p-eminoph

The substance was prepared from 1.12 g of 2-phenylazo (zolylazo) phenyl]-1,3,4-thi

RESULTS and DISCUSSION

In our previous paper we described the preparation of the compound without a catalyst: an easy hydrogenolysis under usual hydrogenation equilibrated in high purity.

In the present investment of 2-aryl/alkylami zolylazo)phenyl]-1,3,4-thi the formation of two prod
from 1.03 g of 2-allylaminophenyl-5-[p-(1-phenyl-3,5-dimethyl-4-pyrazolylazo)phenyl]-1,3,4-thiadiazole (Pale yellow needles).

2 n-Buthylaminophenyl-5 (p-aminophenyl) 1, 3, 4 thiadiazole (II)

The substance was prepared according to the general method from 1.07 g of 2-n-buthylaminophenyl-5-[p-(1-phenyl-3,5-dimethyl-4-pyrazolylazo)phenyl]-1,3,4-thiadiazole (White needles).

2 Cyclohexylaminophenyl-5 (p-aminophenyl)-1, 3, 4 thiadiazole (III)

The substance was prepared according to the general method from 1.14 g of 2-cyclohexylaminophenyl-5-[p-(1-phenyl-3,5-dimethyl-4-pyrazolylazo)phenyl]-1,3,4-thiadiazole (White needles).

2 Phenethylaminophenyl-5 (p-aminophenyl)-1, 3, 4 thiadiazole (IV)

The substance was prepared according to the general method from 1.2 g of 2-phenethylaminophenyl-5-[p-(1-phenyl-3,5-dimethyl-4-pyrazolylazo)phenyl]-1,3,4-thiadiazole (White needles).

2-Phenyl-5 (p-aminophenyl) 1, 3, 4 thiadiazole (V)

The substance was prepared according to the general method from 1.12 g of 2-phenylaminophenyl-5-[p-(1-phenyl-3,5-dimethyl-4-pyrazolylazo)phenyl]-1,3,4-thiadiazole (White needles).

RESULTS and DISCUSSION

In our previous paper, 4-aminopyrazole derivatives were prepared by reducing the azopyrazole derivatives with hydrazine hydrate without a catalyst in ethanol (3-5). This method provides an ease for the resolution with good yield without the need of the usual hydrogenation equipment. The aromatic amines have been isolated in high purity.

In the present investigation, as shown in scheme 1, the treatment of 2-aryl/alkylaminophenyl-5-[p-(1-phenyl-3,5-dimethyl-4-pyrazolylazo)phenyl]-1,3,4-thiadizoles with hydrazine hydrate resulted the formation of two products.
When the reaction medium was diluted water, compounds I-V were obtained, and then when the mother liquor was extracted with chloroform, compound VI was also isolated.

\[
\begin{align*}
R-N-S-N-N=\text{C}_6\text{H}_5 \quad & \text{H}_3\text{C} \quad \text{H}_3\text{C} \quad \text{H}_3\text{C} \\
\text{H}_2\text{N} \quad \text{NH}_2 \quad & \quad \text{N}_2 \\
\text{H}_2\text{N} \quad \text{NH}_2 \\
\text{H}_3\text{C} \quad \text{N} \quad \text{N} \quad \text{C}_6\text{H}_5 \\
\text{H}_3\text{C} \quad \text{N} \quad \text{N} \quad \text{C}_6\text{H}_5 \\
\text{H}_2\text{N} \quad \text{NH}_2
\end{align*}
\]

Scheme – 1

The starting substance of I contains an allyl group. When the NMR spectrum of compound I was investigated, it was found that allyl group was also reduced with hydrazine hydrate to propyl group (Fig. 1).

![NMR Spectrum](image_url)

**Fig. – 1 : NMR Spectrum of 2-n-Propylamino-5-(p-aminophenyl)-1,3,4-thiadiazole (I).**

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>n-C$_4$H$_7$</td>
<td>68</td>
</tr>
<tr>
<td>II</td>
<td>n-C$_5$H$_9$</td>
<td>56</td>
</tr>
<tr>
<td>III</td>
<td>C$_4$H$_8$</td>
<td>41</td>
</tr>
<tr>
<td>IV</td>
<td>CH$_3$CH$_2$C$_2$H$_4$</td>
<td>54</td>
</tr>
<tr>
<td>V</td>
<td>C$_3$H$_2$</td>
<td>59</td>
</tr>
</tbody>
</table>

The IR spectra of I, I' of –NH$_2$ asymetric and shift cm$^{-1}$ in addition to the o of II and III contained characteristic band of –I$^-$

The –NH$_2$ protons at 3.10-5.10 ppm. The other 1
ed water, compounds I-V were extracted.

Table I: Same characteristics of 2-arylalkyl-
amino-3-(p-aminophenyl)-1,3,4-thiadiazole derivatives.

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>Yield %</th>
<th>Molecular Formula</th>
<th>m.p. °C (EtOH)</th>
<th>Analysis Calculated/Found C H N</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>n-C₇H₁₅</td>
<td>68</td>
<td>C₁₁H₁₄N₂S</td>
<td>118-9°</td>
<td>56.38 6.02 23.91</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>56.25 5.79 23.85</td>
</tr>
<tr>
<td>II</td>
<td>n-C₆H₁₃</td>
<td>56</td>
<td>C₁₃H₁₆N₂S</td>
<td>82-4°</td>
<td>56.06 6.65 21.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1/2 H₂O</td>
<td></td>
<td>56.06 7.22 21.70</td>
</tr>
<tr>
<td>III</td>
<td>C₆H₁₁</td>
<td>41</td>
<td>C₁₃H₁₆N₂S</td>
<td>99-101°</td>
<td>57.50 6.89 19.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H₂O</td>
<td></td>
<td>57.57 6.37 18.74</td>
</tr>
<tr>
<td>IV</td>
<td>CH₃-CH₂C₆H₅</td>
<td>54</td>
<td>C₁₅H₂₀N₂S</td>
<td>139-40°</td>
<td>64.83 5.44 18.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>65.17 5.54 18.87</td>
</tr>
<tr>
<td>V</td>
<td>C₆H₃</td>
<td>59</td>
<td>C₁₅H₂₀N₂S</td>
<td>188-9°</td>
<td>62.66 4.58 20.88</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>62.73 4.96 20.79</td>
</tr>
</tbody>
</table>

The IR spectra of I, IV and V showed the characteristic bands of —NH₂ asimetric and simetric stretching vibration at 3320-3286 cm⁻¹ in addition to the other characteristic bands. The IR spectra of II and III contained water of cristalization not showed the characteristic band of —NH₂ streching vibration. (Fig. 2 6).

The —NH₂ protons of I-V appeared as a broad singlet at δ 3.10-5.10 ppm. The other NMR spectral data are listed in Table II.
Table II: UV and NMR. Data of 2-aryl/alky-amino-5-(p-amino-phenyl)-1,3,4-thiadiazole derivatives.

<table>
<thead>
<tr>
<th>Compound</th>
<th>U.V. (EtOH) λmax (nm) g (log)</th>
<th>1H NMR (CDCl₃ + DMSO/TMS) δ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>327 (4.438)</td>
<td>0.98 (1.3H,CH₃); 1.63 (m,2H,CH₂); 3.33 (t,2H,CH₃-N); 3.99-4.50 (br. peak, 2H, NH₂); 6.98 (d,2H_arom., J = 8.5 Hz); 6.59-7.38 (br. peak, 1H, NH); 7.51 (d, 2H_arom., J = 8.5 Hz).</td>
</tr>
<tr>
<td>II</td>
<td>327 (4.398)</td>
<td>0.75-1.83 (m,7H,CH₃,CH₂-CH₃); 3.10-3.70 (4H, CH₂-N and NH₂, br. peak, exchanged with D₂O); 5.99-6.59 (br. peak, 1H, NH); 6.70 (d,2H_arom., J = 8.5 Hz); 7.58 (d,2H_arom., J = 8.5 Hz).</td>
</tr>
<tr>
<td>III</td>
<td>328 (4.459)</td>
<td>0.90-2.40 (m,10H, cyclohexyl); 2.83-3.70 br. peak, 5H, CH₂,N,NH₂,OH); 5.10-5.90 (br. peak, 1H,NH); 6.63 (d,2H_arom., J = 8.5 Hz); 7.58 (d,2H_arom., J = 8.5 Hz).</td>
</tr>
<tr>
<td>IV</td>
<td>325 (4.469)</td>
<td>2.96 (t,2H,CH₂); 3.63 (t,2H,CH₂-N); 4.33-4.83 (br. peak, 2H,NH); 6.88 (d,2H_arom., J = 8.5 Hz); 7.16 (br. peak, 1H,NH); 7.29 (s,3H,C₆H₃); 7.58 (d,2H_arom., J = 8.5 Hz).</td>
</tr>
<tr>
<td>V</td>
<td>239 (Shoulder) 344 (3.811)</td>
<td>3.90-5.10 (br. peak, 2H,NH₂); 6.70 (d, 2H_arom., J = 8.5 Hz); 6.90-7.70 (m,8H,NH, C₆H₃ and 2H_arom.).</td>
</tr>
</tbody>
</table>
IR (CDCl$_3$ + DMSO/TMS)
\( \delta \) (ppm)

1.63 (m, 2H, CH$_2$); 3.33 (t, 2H, CH$_2$-N);
k, 2H, NH$_2$): 6.58 (d, 2H$_{arom}$, \( J = 8.5 \) Hz).

- peak, (H, NH): 7.51 (d, 2H$_{arom}$).

H$_2$CH$_2$CH$_3$): 3.10-3.70 (d, CH$_2$-N

ark, exchanged with D$_2$O): 3.90-5.50

): 6.70 (d, 2H$_{arom}$, \( J = 8.5 \) Hz); 7.58

8.5 Hz).

- cycloheptyl): 2.83-3.70 br. peak, 5H.

: 5.10-5.90 (br. peak, (H, NH): 6.65

8.5 Hz; 7.58 (d, 2H$_{arom}$; \( J = 8.5 \) Hz).

: 3.63 (t, 2H, CH$_2$-N); 4.33-4.83 (br.

1.68 d, 2H$_{arom}$, \( J = 8.5 \) Hz); 7.16 (br.

7.26 (s, 2H, C$_2$H$_6$); 7.53 (d, 2H$_{arom}$).

\( \delta \) (ppm)

2H, NH$_2$): 6.70 (d, 2H$_{arom}$; \( J = 8.5 \)
m, 8H, NH, C$_2$H$_6$, and 2H$_{arom}$.

Fig. 2: IR Spectrum of 2,4-Pyrimidine-5-(p-aminoanilino)-1,3,4-thiadiazole (1).

Fig. 3: IR Spectrum of 2-n-Bulylamino-5-(p-aminoanilino)-1,3,4-thiadiazole (11).
REFERENCES


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2 species of Antheric
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ledge, distributional m
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miş ve 1976 1982 yıla

(*) M.U. Eczacılık Fakültesi.